

Conclusions

Measurements of the rates of reaction of carbon dioxide with both artificial and natural graphite and with several high temperature cokes of known history have been reported. The results have been calculated to give the reaction rates per unit volume of coke or graphite and have been corrected for the perfusion of the reacting gas throughout the body of the porous samples. Because of this manipulation, the results are not particularly precise, errors of the order of 20% being possible.

It is shown that artificial graphites and cokes behave, in reaction, like porous bodies whose internal surface contributes to the reaction rate. The reaction of carbon dioxide with artificial graphite has a temperature coefficient corresponding to a heat of activation of about 52 kcal. That of the reaction with natural graphite is more uncertain because of the marked effect of the mineral impurities which the sample contained, but it appears to be of the order of 44 kcal.

PITTSBURGH, PENNSYLVANIA RECEIVED MAY 31, 1939

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Colorimetric Determination of Palladium with *p*-Nitrosodiphenylamine¹

BY JOHN H. YOE AND LYLE G. OVERHOLSER

The colorimetric methods available for the determination of palladium have been developed in connection with platinum analysis,^{2,3} and while they do provide rapid and accurate methods for the determination of quantities of palladium of the order of 0.1 mg., no colorimetric method has been reported that will yield reasonably accurate results with quantities of the order of a few γ . Studies have been made on reagents for the detection and approximate estimation of minute quantities of palladium. *p*-Dimethylaminobenzylidene rhodanine⁴ has been used for the detection of palladium, but no application of this reagent for the quantitative determination of the metal has been reported. This reagent is extremely sensitive for palladium but not so nearly specific as *p*-nitrosodiphenylamine. Feigl and Fränkel⁵ report that as little as 0.0025 γ of palladium per ml. (1:400,000,000) can be detected by the catalytic effect of palladium on the reduction of nickel salts by sodium hypophosphite. Pierson⁶ utilized the reducing action of mercurous chloride for the de-

tection and approximate estimation of minute quantities of the metal by observing the shades of color produced by the adsorbed metal. But there is need of a method that may be used for the determination of minute quantities of palladium and that is not rendered useless by the presence of the other metals frequently accompanying palladium.

p-Nitrosodiphenylamine has been found to react with palladous chloride in neutral and weakly acid solution to give either a deep red colored solution or a purplish-brown precipitate, depending on the concentration of the metal. The reaction is extremely sensitive, permitting the detection of 0.005 γ of palladium by the spot-plate technique, and compares favorably with *p*-dimethylaminobenzylidene rhodanine. The reagent is practically specific for palladium, in the sense that the only other metals forming colored compounds are gold and silver. The sensitivity for gold and silver, however, is much less than for palladium. Oxidizing agents interfere by giving colored solutions; cyanides and iodides prevent the formation of the colored compound. The sensitivity is affected by the pH of the solution and the concentration of salts present, but these can be controlled easily.

If the reagent is added in excess to a weakly acidic palladous chloride solution, the palladium is quantitatively precipitated. On the other hand, if a sodium acetate-hydrochloric acid buffer of the proper pH and salt concentration is used, a deep red colored solution results which may

(1) This investigation was partly supported by a grant-in-aid from the Carnegie Corporation. It is the first of a projected series based upon studies of inorganic reagents in organic analysis. These studies are being conducted as a cooperative effort in which eight Virginia institutions are participating under the direction of John H. Yoe. Those cooperating with the University of Virginia are: Hampden-Sydney, Mary Baldwin, Randolph-Macon (Ashland), Virginia Military Institute, Virginia Polytechnic Institute, Washington and Lee, and William and Mary.

(2) O. E. Zvyagintzev, *Ann. inst. platine*, 364 (1926).

(3) F. C. Robinson, *Bull. Am. Inst. Mining Met.*, No. 260 (1926).

(4) F. Feigl, P. Krumholz and E. Rajmann, *Mikrochemie*, **9**, 165 (1931); H. Holzer, *ibid.*, **8**, 271 (1930).

(5) F. Feigl and E. Fränkel, *Ber.*, **65B**, 539 (1932).

(6) G. C. Pierson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 437 (1934); *ibid.*, **11**, 86 (1939).

be satisfactorily used for the colorimetric determination of palladium in the range 0.5–50 γ .

This paper presents various aspects of the new reaction, details for the colorimetric method, and procedures for the determination of palladium when accompanied with gold and platinum.

Materials Used

Palladium Chloride.—A stock solution was prepared by dissolving a 1.74-g. sample of palladous chloride (57.5% of palladium) in 85 ml. of hydrochloric acid and diluting to 1 liter with water. This gave a solution 1 *M* with respect to hydrochloric acid and contained 1.003 mg. of palladium per ml. as determined by analysis with dimethylglyoxime. Solutions containing 1 and 10 p. p. m. of palladium, respectively, were prepared by diluting the stock solution with water.

Acids.—Unless otherwise indicated, all acids used in this study were concentrated c. p. reagents.

***p*-Nitrosodiphenylamine.**—The product used was obtained from the Eastman Kodak Company and had a m. p. of 143–144°. A solution of the reagent was prepared by dissolving 50 mg. of the solid in 500 ml. of 95% ethyl alcohol and diluting to 1 liter with water. This solution had a yellowish-orange color and was stable for several months.

Sodium Acetate–Hydrochloric Acid Buffer.—This buffer solution was prepared by adding 240 ml. of 1 *M* hydrochloric acid to 200 ml. of 1 *M* sodium acetate and diluting the mixture to 1 liter with water. The *pH* of the solution, as measured by the quinhydrone electrode, was 1.6. Upon diluting 25 ml. of this buffer to 100 ml. with water a *pH* value of 2.1 was obtained.

Procedure Recommended for the Determination of Small Quantities of Palladium.—The method may be applied successfully to the determination of quantities of palladium not exceeding 50 γ , although it is preferable that the amount present be less than 30 γ . Palladium may be determined in such materials as crude platinum and the various alloys, provided interfering substances are first removed. Directions are given in another section for the separation from platinum and gold, since these metals frequently accompany palladium. Palladium may be determined in the presence of iridium and rhodium, provided the ratio of iridium to palladium and that of rhodium to palladium does not exceed 20 to 1.

Several precautions must be observed in order to obtain reliable results. The palladium should be present as palladous chloride in a solution containing not more than 0.5 mmol. of hydrochloric acid or a total salt concentration of not over 3 mmol. The reagent should be added to all solutions (unknowns and standards) at as nearly the same time as possible (within fifteen minutes), and all the solutions should be at room temperature when the reagent is added. Finally, the matching should be completed within one hour after the addition of the reagent.

Procedure.—Prepare the standard series by using the following increments of palladium in the respective concentration ranges: 0–10 γ , 0.5 γ ; 11–25 γ , 1 γ ; 26–35 γ , 2 γ ; 36–50 γ , 5 γ . Transfer the solutions containing the palladous chloride (standards and unknowns) to 100 ml.

volumetric flasks, add 25 ml. of the sodium acetate–hydrochloric acid buffer from a pipet, 2 ml. of reagent from a pipet, and dilute to 100 ml. with water. Before matching the solutions, thoroughly mix and allow them to stand at room temperature for about thirty minutes.

Color matching in our work was done with a roulette comparator⁷ using 100-ml. tubes (160 mm.). At the lower palladium concentrations, Corning Filter no. 512 was used advantageously, while filters nos. 585 and 556 were employed at the higher concentrations. In some cases the matching was also carried out in 50-ml. Nessler tubes (220 mm.). The latter method is as sensitive at the lower concentrations but less so at the higher ones, because filters are not applicable. Since the observed color is a mixture of the yellow color of the reagent and that of the red palladium compound, the Duboscq colorimeter is of little use due to the change in the shade of color obtained with different amounts of palladium. The photoelectric colorimeter may be used but no increase in the actual sensitivity is obtained because of the influence of several uncontrollable factors.

Experimental Development of the Procedure

Reaction of *p*-Nitrosodiphenylamine with Palladous Chloride.—The greatest difficulty encountered during the development of the method was the formation of turbid solutions. In unbuffered as well as with biphthalate buffers, turbid solutions always resulted. The sodium acetate–hydrochloric acid buffers were unique because they gave clear red solutions, when buffers having a relatively high salt concentration and a low *pH* were used. If more than 2 ml. of the reagent was used, however, turbid solutions were obtained, even in the presence of the prescribed buffer medium.

A sample of the solid compound was obtained in the following manner: 50 ml. of a solution of palladous chloride containing 50 mg. of palladium was diluted to 500 ml. with water. To this solution was added 50 ml. of a filtered alcoholic solution containing 100 mg. of *p*-nitrosodiphenylamine. The precipitate was filtered off, dried for twelve hours at 110° and analyzed. *Anal.* Calcd. for $C_{24}H_{20}N_4O_2PdCl_2$: C, 50.21; H, 3.51; Pd, 18.59; Cl, 12.35. Found: C, 50.15; H, 3.85; Pd, 18.52; Cl, 12.21.⁸

The composition corresponds to the formula $Pd[C_6H_5-NHC_6H_4NO]_2Cl_2$, which is a coordination compound analogous to the other numerous ammino compounds of palladium, exemplified by $Pd(NH_3)_2Cl_2$. Palladous nitrate also reacts with the reagent to give a compound having a similar color which is probably an analogous coordination compound.

The sample analyzed was precipitated from a solution containing an excess of palladium, because the precipitate so obtained was handled more easily than that obtained by using an excess of the reagent. Samples were also prepared by using an excess of reagent, as well as by precipitating the palladium from a sodium acetate–hydrochloric acid buffer under the same conditions used in the colorimetric procedure. In these samples, only palladium was

(7) J. H. Yoe and T. B. Crumpler, *Ind. Eng. Chem., Anal. Ed.*, **7**, 78 (1935).

(8) The authors are indebted to Miss Elizabeth C. Johnson of this Laboratory for the halogen determination.

determined but the values obtained checked that of the compound reported above, leaving no doubt that the samples prepared in the different ways all had the same composition.

The compound appears as a purplish-brown amorphous precipitate which adheres tenaciously to glassware and is very difficult to filter. It loses water slowly when dried at 110° , but if heated above 120° it undergoes a very gradual decomposition. The compound is insoluble in water but moderately soluble in 95% ethyl alcohol, yielding a deep red colored solution. It dissolves in moderately strong hydrochloric, nitric, or sulfuric acid, giving solutions ranging in color from red to yellow. With ammonia and sodium hydroxide, yellow solutions are formed.

Although the composition of the precipitate is satisfactorily constant and has the advantage of a low palladium content, the difficulties encountered in filtering and drying prevent it from having a practical value in gravimetric analysis, especially since other more suitable organic precipitants are available.

The relative absorption curves for solutions of the reagent and of the palladium compound are given in Fig. 1.

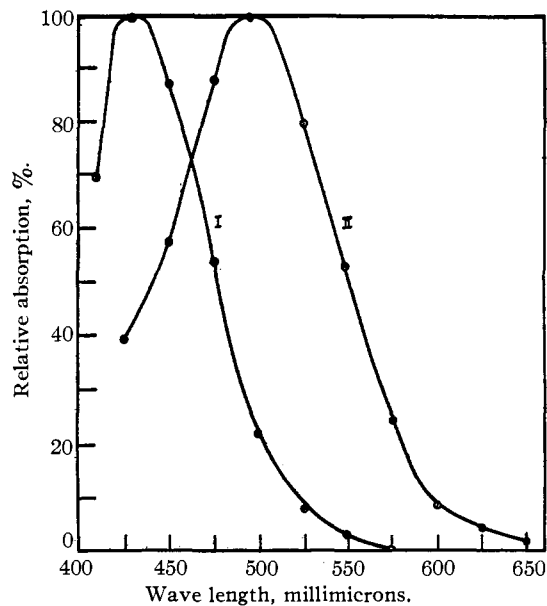


Fig. 1.

The data for the curves were obtained with a photoelectric spectrophotometer.⁹ Curve I, the reagent curve, was obtained for a solution prepared by adding 10 ml. of the reagent to 25 ml. of standard buffer solution and diluting to 100 ml. with water (pH 2.1). Curve II, the compound curve, was obtained for a solution containing 70 γ of palladium prepared in the same manner as for the colorimetric determination. It will be observed that the maximum for the reagent and that for the compound occur near each other. Consequently, it is difficult to eliminate, by the use of a color filter, the absorption by the reagent.

Effect of Concentration of Salts.—The presence of small amounts of salts, such as sodium chloride, have a marked

effect on the reaction when carried out in solutions of low ionic strength. For example, using 5 γ of palladium and a final concentration of hydrochloric acid of 10^{-4} or 10^{-5} M it was found that as small a concentration of sodium chloride as 10^{-4} M caused a slight decrease in the intensity of the color. With larger amounts of sodium chloride, a corresponding decrease in the red color was observed and with a concentration as great as 1 M practically none of the red colored compound formed. Other sodium salts such as the nitrate and sulfate, as well as the corresponding potassium and ammonium salts, exhibit a similar behavior.

Under the conditions recommended, *i. e.*, the use of a buffer with a final salt concentration of 0.05 M , the maximum color or sensitivity is not obtainable because of the salt effect. It is necessary to use the buffer to prevent turbidity, and to minimize the effect of additional salts, as well as to control the pH . In the buffer system used, the presence of additional salts in amounts to give a final concentration of 0.01 M is without effect and the maximum concentration allowable without error is 0.03 M .

Effect of Hydrogen-Ion Concentration.—The intensity of the color of the reagent and that of the palladium compound depends upon the pH of the solution. The reagent exhibits a yellowish-orange color of maximum intensity at a pH of 5 to 6. Above or below these values the intensity of the color decreases, attaining a pale yellow in strongly acidic and basic solutions. The intensity undergoes a pronounced change in the pH region in which the determinations are carried out, a change of 0.2 of a pH unit giving a difference in color just detectable.

The formation of the colored palladium compound does not occur in strongly acidic or basic solutions. In sodium acetate buffers having a salt concentration of 0.05 M , the intensity of the red color increases from a pH of 1.7 to 3, where it attains a maximum and then decreases. The change is more pronounced from a pH of 1.7 to 3 than from 3 to 5. The maximum sensitivity appears to be at a pH of 3, but as the ionic strength of the buffers differed, part of the effect attributed to pH may be due to the salt effect. Using 20 γ of palladium, it was found that turbid solutions resulted in all cases where the pH was greater than 2.1. Thus the method is limited to a narrow pH range, as well as being confined to the sodium acetate-hydrochloric acid buffers. The pH of 2.1 was selected for the method as it affords the maximum sensitivity without producing turbid solutions. The solutions are reasonably well buffered. The equivalent of 0.5 ml. of 1 M hydrochloric acid may be present without causing any visible change in color intensity and 0.75 ml., which is the maximum allowable, causes no serious error. The latter amount of acid produces a pH change of 0.2 unit as measured by the quinhydrone electrode. The presence of equivalent amounts of nitric acid produces a similar effect.

Formation and Stability of Color.—The effect of salts and of the hydrogen-ion concentration on the extent of the development of the color has just been considered. An increase in the amount of salts present or a decrease in the pH of the solution causes an increase in the time required for development of the maximum color. Usually, under the conditions giving maximum sensitivity, the development of the color is nearly instantaneous but turbid solutions result. In the colorimetric procedure which

(9) Description of this instrument to be published soon by Barton and Yoe.

yields clear solutions, the development is slow, about thirty minutes being required for the attainment of maximum intensity.

With an increase of temperature, the rate of development increases markedly, but above 50 or 60° the color fades completely. Temperature changes seem to affect only the rate of development and not the final maximum intensity. Although a temperature difference of 5° is noticeable, no special precautions are required other than that the solution be at room temperature when the reagent is added.

All solutions of the colored compound tend to give a precipitate upon aging. Under the conditions used in the method, the clear solutions are reasonably stable for several hours, but upon longer standing they fade and give a precipitate. Because of this limited stability, it is necessary that the reagent be added to all solutions at as nearly the same time as is possible and that the matching be completed within one hour after the addition of the reagent. These conditions are especially important with quantities of palladium exceeding 10 γ .

The colors obtained are satisfactorily reproducible and the order of addition, *i. e.*, reagent to palladium and buffer or palladium to reagent and buffer, has no effect.

Interference of Other Elements.—No reaction between the reagent and any of the following ions was observed. The tests were made on a spot-plate by adding a drop of the reagent to a drop of the solution containing the respective ions (approx. 0.05 mg.). Ions tested: Al³⁺, As³⁺, AsO₄⁻³, B₄O₇⁻², Ba²⁺, Be²⁺, Bi³⁺, Br⁻, CO₃⁻², Ca²⁺, CbO₄⁻³, Cd²⁺, Ce³⁺, Cl⁻, Co²⁺, Cr³⁺, Cs⁺, Cu²⁺, Dy³⁺, Er³⁺, Eu³⁺, F⁻, Fe²⁺, Fe³⁺, Ga³⁺, Gd³⁺, Ge⁴⁺ (aqueous solution of GeO₂), Hf⁴⁺(HfO⁺²), Hg²⁺, I⁻, In³⁺, Ir⁴⁺, K⁺, La³⁺, Li⁺, Mg²⁺, Mn²⁺, MoO₄⁻², NO₂⁻, NO₃⁻, Na⁺, Nd³⁺, Ni²⁺, OsO₆⁻², HPO₄⁻², Pb²⁺, Pr³⁺, Rb⁺, ReO₄⁻, Rh³⁺, Ru³⁺, S⁻², SO₄⁻², Sb³⁺, Sc³⁺, SeO₃⁻², SiO₃⁻², Sm³⁺, Sn²⁺, Sn⁴⁺, Sr²⁺, TaO₄⁻³, TeO₄⁻², Ti⁴⁺ (Ti₂O⁺⁶ or TiO⁺²), Th⁴⁺, Tl³⁺, Tm³⁺, UO₂⁺², VO⁺, WO₄⁻², Y³⁺, Yb³⁺, Zn²⁺, Zr⁴⁺(ZrO⁺²).

The auric ion reacts with the reagent to form a purple colored solution. The reaction is not as sensitive as that for palladium, but the presence of gold in amounts exceeding 1 p. p. m.¹⁰ interferes with the method and must be removed.

The first solution of platonic chloride tested yielded a slight red coloration. Later it was found that palladium was present as an impurity, and a subsequent test with a pure solution gave no color reaction. After standing for several hours in direct sunlight, however, platinum does react to give a very faint coloration; after several days an intense red color is formed that may serve as a sensitive test for platinum. Under the conditions of the method, however, platinum does not interfere, except by its color which becomes troublesome at concentrations exceeding 20 p. p. m.

In neutral solution, silver ions react with the reagent to give a red precipitate. The reaction is not sensitive, nor does it occur in acid solution. However, because it is necessary to use a buffer containing hydrochloric acid, silver must be absent to prevent turbid solutions due to silver chloride.

Ceric and bromate ions as well as other strong oxidizing agents interfere. Substances reacting with the palladous ion such as iodide, cyanide, and strong reducing agents, must necessarily be absent.

With the exception of silver and mercurous ions, colorless metallic ions do not interfere. The following were tested at a concentration of 100 p. p. m. and found to be without effect: Al, Cd, Hg²⁺, Mn²⁺, Pb, and Zn.

The following colored ions interfere only when present in large enough amounts to produce an interfering color. The ions and limiting concentrations are: Co, 10 p. p. m.; Cu, 50; Fe³⁺, 30; Ir, 2; Ni, 25; Rh, 2.

Separation of Gold from Palladium.—Gold in excess of 1 p. p. m. must be removed, for it interferes seriously with the method. The removal was attempted unsuccessfully by reduction to the metal with oxalic acid. A single precipitation of the gold resulted in a loss of most of the palladium; a reprecipitation, although improving the separation, did not make it quantitative. Repeated precipitations perhaps would give a satisfactory separation, but such operations are tedious and since another satisfactory method was available, the former method was discarded. Gold may be removed satisfactorily by extraction with either ethyl acetate¹¹ or ether¹² from a solution containing hydrochloric acid. The following procedure is satisfactory for the removal of gold.

Procedure.—Add sufficient hydrochloric acid to the solution (volume of 15 ml. or less) containing auric and palladous chlorides to give a final concentration of approximately 10%. Transfer the solution to a small separatory funnel, add 10 ml. of ethyl acetate (or ether), shake for a few seconds and draw off the acid layer. Shake the ethyl acetate layer with a few ml. of 10% hydrochloric acid and combine the wash solution with the other acid portion. If necessary, repeat the extraction with another 10-ml. portion of ethyl acetate. Evaporate the solution to dryness on the steam-bath, take up the residue in a few ml. of hydrochloric acid and evaporate almost to dryness (no more than a drop remaining). Add water and determine palladium by the standard procedure.

The results given in Table I were obtained for solutions containing varying amounts of auric and palladous chlorides. The removal of gold has been sufficiently complete to avoid interference in all cases except in the experiments in which the solutions containing 5 mg. of gold

TABLE I

Extractions	Au added, mg.	Pd added, γ	Pd found		Au/Pd
			Ethyl acetate γ	Ether γ	
1	1	5.0	4.5	5.0	200
1	5	10.0	10.0	11.0 ^a	500
2	10	20.0	19.0		500
1	5	5.0	5.0	6.0 ^a	1000
2	10	10.0	9.5	9.5	1000
2	10	5.0	4.5	5.0	2000
2	15	5.0	4.5	5.0	3000
2	20	5.0	4.5		4000
3	50	5.0	5.0	5.5	10000

^a High results were due to the interference of gold.

(10) This and similar notations refer to a volume of 100 ml. and a solution height of 160 mm.

(11) V. Lenher and C. H. Kao, *J. Phys. Chem.*, **30**, 126 (1926).

(12) F. Mylius, *Z. anorg. Chem.*, **70**, 203 (1911).

were extracted only once with ether and a satisfactory recovery of palladium resulted even where the ratio of gold to palladium was 10,000:1. Ether appears to be the more suitable extractant, yielding slightly higher results in most cases than those obtained with ethyl acetate and if a complete removal of gold is not required it would be preferable. Ethyl acetate is, however, a more efficient extractant; if the most nearly complete removal of gold with the least number of extractions is desired, it is preferable to ether.

Separation of Palladium from Platinum.—Amounts of platinum exceeding 2 mg. produce an interfering yellow color, making it necessary to separate the two metals. The removal of platinum was attempted by precipitation with ammonium chloride. This method was found to be entirely unsatisfactory, resulting in the loss of most of the small amounts of palladium present. Even the use of solutions not saturated with ammonium chloride, and which did not give a quantitative precipitation of platinum, gave unsatisfactory results. The reaction between stannous chloride and platinic chloride in hydrochloric acid and the subsequent extraction with ether¹³ or ethyl acetate¹⁴ was also employed. This method was not satisfactory, the loss of palladium perhaps being caused by the presence of hydrated stannic oxide formed in subsequent operations. Palladium could not be precipitated with dimethylglyoxime at such low concentrations. The use of small amounts of nickel as a collector resulted in a partial precipitation of palladium by dimethylglyoxime. The method finally adopted—which involved the precipitation of palladium as the hydrated dioxide as given by Gilchrist and Wichers¹⁵—gave a very satisfactory separation. This method gives a remarkably clean-cut separation of extremely small amounts of palladium from relatively large amounts of platinum. In our experiments, a small amount of iron was used as a collector, though it was later found that as little as 5 γ of palladium could be separated without the use of a collector. The procedure given is that of Gilchrist and Wichers¹⁵ applied to small quantities of the metals.

Procedure.—Add 0.2 ml. of ferric nitrate (0.2 mg. of iron) to the solution containing platinum and palladium, a few ml. of hydrochloric acid, and approximately 100 mg. of sodium chloride. Evaporate the solution to dryness, add hydrochloric acid, and once more evaporate to dryness. Add 4–5 drops of hydrochloric acid and 40 ml. of water, heat the solution to boiling and add 2 ml. of a filtered 10% sodium bromate solution. Then add dropwise a 10% solution of sodium bicarbonate until cresol red turns pink. (Test a drop of solution on the stirring rod with the indicator.) Add 2 ml. of the sodium bromate solution and boil for fifteen minutes. Filter through a fritted glass funnel or crucible, wash the precipitate several times with a few ml. of a 1% sodium chloride solution, having a pH of 6 or 7, dissolve the precipitate in 5 ml. of hydrochloric acid, and wash the filter with water. Evaporate the solution to dryness on the steam-bath, add a few ml. of hydrochloric acid, evaporate almost to dryness (not more than a drop) and take up in water. Deter-

mine the palladium in this solution by the standard procedure.

The results obtained by using this procedure for the analysis of solutions containing palladium and platinum were entirely satisfactory. For instance, in an experiment using 20 mg. of platinum and 5 γ of palladium, all the palladium was found. In another set with 20 mg. of platinum and 2 γ of palladium (ratio of Pt/Pd = 10,000), 2 γ of palladium was recovered. The method may be extended to even greater ratios by using larger amounts of platinum.

The method was applied to the analysis of metallic platinum samples. The samples were dissolved in *aqua regia*, the nitric acid removed by repeated evaporation with hydrochloric acid in the presence of sodium chloride and the residues taken up in water. The palladium was then determined. One sample contained 0.09% of palladium; another contained less than 0.002%, this being the limit of sensitivity with a 20-mg. sample.

Several experiments were also run in which palladium was determined in solutions containing the chlorides of palladium, gold, and platinum. The gold was removed by extraction with ethyl acetate and the palladium then determined after separation from platinum by the method given above. Satisfactory results were obtained in all experiments.

Separation of Silver from Palladium.—In the analysis of materials containing silver and "platinum group" metals, silver is usually removed as the chloride and would not be found in the solution prepared for the analysis of palladium. It was of interest, however, to determine whether or not small amounts of palladium might be carried down with the silver chloride. Accordingly, a few experiments were performed in which silver was precipitated as the chloride in the presence of small amounts of palladium. The general procedure followed was to take solutions containing known amounts of silver and palladium, dilute to 100 ml., acidify with nitric acid and precipitate the silver with hydrochloric acid. Each solution was filtered through a fritted glass crucible, the precipitate washed well with very dilute hydrochloric acid and palladium determined in the filtrate by the standard procedure, after the removal of nitric acid by repeated evaporation with hydrochloric acid in the presence of a few mg. of sodium chloride.

The results showed that palladium was lost in the separation. For example, using 20 mg. of silver and 10 γ of palladium only 7.5 γ of palladium was found. In several instances the silver chloride was dissolved in ammonium hydroxide, the filter thoroughly washed and then treated with *aqua regia*. Part of the palladium was recovered by this treatment, indicating that a partial reduction of the palladous ion to the metallic state had occurred. This reduction was probably due to the presence of a small amount of metallic silver formed by the action of light. This does not account, however, for all the palladium lost, and it seems probable that the loss is, at least in part, due to occlusion or adsorption by the silver chloride. Prolonged digestion or a reprecipitation afforded little or no improvement in the separation.

Sensitivity and Accuracy of the Determination.—Using a spot-plate, 0.005 γ of palladium (0.05 ml. of a solution containing 1 part of Pd in 10,000,000) may be detected.

(13) E. Langstein and P. H. Prausnitz, *Chem.-Ztg.*, **38**, 802 (1914).

(14) H. W. Wöbling, *Ber.*, **67B**, 773 (1934).

(15) R. Gilchrist and E. Wichers, *THIS JOURNAL*, **57**, 2565 (1935).

The paper spot method is sensitive to about 0.01 γ . In solutions of extremely low ionic strength, as little as 1 part of palladium in 300,000,000 parts of solution may be detected in 50-ml. Nessler tubes (220 mm.). Under the conditions in which the determinations are carried out, the concentration limit is 1:200,000,000, using either Nessler tubes or the roulette comparator. This corresponds to 0.25 γ of palladium with the former and 0.5 γ with the latter. The method may be made more sensitive by the use of smaller volumes. For instance, using 2 ml. of solution in small test-tubes which gave a column of liquid 50 mm. in height, 0.04 γ was detectable. With 10 ml. of solution and a column height of 80 mm., 0.1 γ was detectable.

The accuracy of the determination depends upon the concentration of palladium present, the volume of solution used, the method of matching, and the presence or absence of interfering substances. The accuracy reported below for the different amounts of palladium is based on a volume of 100 ml. using a roulette comparator (100 ml. tubes, 160 mm. to mark) with a Corning Filter no. 512 for amounts of palladium up to 20 γ and Filter no. 585 for larger amounts. The accuracy found under the most favorable conditions was as follows: 0.5–10 γ , 0.25 γ ; 10.5–25 γ , 0.5 γ ; 26–35 γ , 1 γ ; 36–50 γ , 2.5 γ .

Acknowledgment.—The authors wish to express their appreciation to Charles J. Barton of this Laboratory for the data used in the relative absorption curves.

Summary

The reaction between *p*-nitrosodiphenylamine and palladous chloride has been described. This reaction is extremely sensitive and nearly specific for palladium. Studies have been made on the effect of salts, of hydrogen-ion concentration, of temperature, and of interfering substances on the color formation and stability of the compound.

The composition of the compound has been determined and found to correspond to the coordination compound $\text{Pd}[\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{NO}]_2\text{Cl}_2$. The compound has a purplish-brown color in the solid state but under the experimental conditions used in the colorimetric procedure it forms a red solution.

Relative absorption curves are given for solutions of the reagent and of the palladium compound.

Details are presented for a new colorimetric method permitting the determination of quantities of palladium of the order of a few γ , as well as results of its application. Procedures are also given for the determination of palladium when accompanied by gold and platinum.

UNIVERSITY, VIRGINIA

RECEIVED APRIL 1, 1939

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Vitrification and Crystallization of Organic Molecules and the Dielectric Behavior of *i*-Butyl and *i*-Amyl Bromides

BY WILLIAM O. BAKER AND CHARLES P. SMYTH

The relation of molecular structure to molecular interaction and rotational freedom in the solid state has been studied by means of dielectric constant and dispersion measurements on a series of molecules of differing shapes. In investigating the connection between the symmetry of the crystal lattice and the symmetry of the molecule, *i*-butyl and *i*-amyl bromides were examined as pear-shaped forms intermediate between the rod-like long¹ chain compounds, and the nearly spherical *t*-butyl halides.² Their ready vitrification permitted analysis of both crystalline and glassy behavior.

A capacity bridge coupled to a low-frequency, variable oscillator, and to a vacuum tube, six-stage amplifier was employed for the dielectric measurements in the same general fashion as that

already described.³ Temperatures were obtained from a platinum resistance thermometer. The crystals and glasses were examined over a wide temperature range with a polarizing microscope equipped with a transparent Dewar tube mounted on the stage. The cell containing the material to be measured was inserted in a brass block into which liquid air could be injected at any desired rate.³ Further the block assembly was suspended in a large Dewar vessel, from the lower portion of which liquid air could be evaporated to provide a very slow rate of temperature change in the cell. The usual care was taken to reduce void formations between the condenser walls by pumping off dissolved gases from the liquid in the cell, by subsequent freezings and meltings, and by slow final freezing from the bottom of the cell upward.

(1) Baker and Smyth, *THIS JOURNAL*, **60**, 1229 (1938).

(2) Baker and Smyth, to be published.

(3) Smyth and Hitchcock, *THIS JOURNAL*, **54**, 4631 (1932); **55**, 1830 (1933).